

(11) EP 0 715 885 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
12.06.1996 Bulletin 1996/24

(51) Int Cl.⁶: B01J 3/06

(21) Application number: 95308793.9

(22) Date of filing: 05.12.1995

(84) Designated Contracting States:
DE FR GB IE

(30) Priority: 05.12.1994 JP 300595/94
09.10.1995 JP 287972/95
30.11.1995 JP 312579/95

(71) Applicant: SUMITOMO ELECTRIC INDUSTRIES,
INC.
Chuo-ku, Osaka (JP)

(72) Inventors:

- Sumiya, Hitoshi, c/o Itami Works of Sumitomo Itami-shi, Hyogo (JP)
- Toda, Naohiro, c/o Itami Works of Sumitomo Itami-shi, Hyogo (JP)
- Satoh, Shuichi, c/o Itami Works of Sumitomo Itami-shi, Hyogo (JP)

(74) Representative: Allard, Susan Joyce et al
BOULT, WADE & TENNANT
27 Funnival Street
London EC4A 1PQ (GB)

(54) A low defect density diamond single crystal and a process for the production of the same

(57) A colourless, transparent low defect density, synthetic type IIa diamond single crystal, in which the etch pits due to needle-shaped defects are at most 3×10^6 pieces/cm², and which can be applied to uses requiring high crystallinity of diamond, for example, monochromators, semiconductor substrates, spectroscopic crystals in X-ray range, electronic materials, etc., is provided by a process for the production of the colourless,

transparent, low defect density, synthetic diamond single crystal by growing new diamond crystal on a seed crystal of diamond by the temperature gradient method which comprises using a crystal defect free diamond single crystal, as a seed crystal of diamond, and optionally subjecting to a heat treatment in a non-oxidizing atmosphere at a low pressure and a temperature of 1100 to 1600°C.

EP 0 715 885 A2

Description

This invention relates to a high quality synthetic diamond single crystal substantially free from crystal defects, strains, etc., which finds application in a variety of fields, such as optical parts, spectroscopic crystals, monochromators, laser windows, anvils, semiconductor substrates, heat resistant semiconductors, device substrates for high power applications, and to a process for the production of the same.

Diamond crystals can be applied to various uses such as heat sinks, dies for wire drawing, cutting tools for precision working, optical parts, laser windows, and anvils for producing ultra-high pressures, due to their high hardness and strength, excellent thermal conductivity and corrosion resistance and good transmittance of light.

Naturally occurring diamonds, most of which are called type Ia, contain about 1000 ppm of nitrogen. The nitrogen in this natural diamond is distributed in the crystal in an aggregated form, resulting in a synthetic number of crystal defects, high internal strains and adsorption of light in the infrared range. Depending upon the variety of the rough stone, considerable dispersion may also arise. Consequently, the applied use has been limited to heat sinks or tools.

High purity natural diamond containing nitrogen impurities in an amount of at most several ppm is called type IIa. Type IIa diamond constitutes an output of only about 2 % based on all rough stones. Since the natural type IIa diamond contains a very small amount of impurities, is colorless and transparent and has superior transmission properties, it has widely been applied to jewellery, optical parts and laser window materials.

However, defects and strains still remain to a considerable extent in the interior part of the natural diamond, because of complicated growth processes which have occurred in the interior part of the earth. Accordingly, natural diamond cannot be applied to uses requiring high crystallinity, for example, monochromators or semiconductor substrates. Furthermore, natural diamond of type IIa suffers to such an extent from strains in the lattice, that the output quantity is small, resulting in high production costs.

An ordinary diamond artificially synthesized under ultra-high pressure and high temperature is called type Ib and contains several hundreds ppm of nitrogen. Since this nitrogen is contained in the diamond crystal as an isolated substitutional impurity, absorption of light due to the nitrogen impurity occurs in the infrared and ultraviolet ranges and the diamond crystal cannot be applied to optical parts or window materials. In addition, the distribution of nitrogen is largely uneven in the interior part of the crystal, resulting in a greater number of defects and high strains in the crystal. The number of needle-shaped defects in the diamond single crystal is at least 10^6 pieces/cm².

It is known that when a nitrogen getter such as Al or Ti is added to a solvent metal during synthesis of diamond, the nitrogen in the diamond can be removed to a level of about several ppm. When the nitrogen getter is added to the solvent metal, however, inclusions in large amounts ordinarily tend to be incorporated into the crystal, thereby decreasing the production yield of good quality crystal. Accordingly, the production cost of the synthetic type IIa diamond is higher than that of the natural type IIa diamond and the production thereof has not been carried out on a commercial scale.

We have now found that an inclusion-free synthetic type IIa diamond having a nitrogen content of at most approximately 0.1 ppm can stably be synthesized by using at least one element selected from Group IVa and Va elements having a high nitrogen removal efficiency as a nitrogen getter and simultaneously controlling so that inclusions are not taken in the crystal.

Up to the present time, diamond has widely been used in jewellery, grinding abrasives, heat sinks, sound vibration plates, etc. Recently, diamond crystals have found application as crystals for use in spectroscopy in the X-ray range and as semiconductor substrates. In these applications, diamond is used under such a state that the excellent properties of diamond are raised to the utmost limits and to this end, a low defect density diamond crystal is required. The low defect density diamond is less in natural crystals. Since it has been reported that diamonds artificially synthesized at a high pressure, in particular, diamond called type IIa, containing a very small amount of impurity, nitrogen, has less defects, the above described artificial diamonds have often been used in the fields needing the low defect diamond. However, at the present time when further low defect density diamond is being required, it is looked out for from the artificial diamonds with relatively low defects and the diamond having such crystallinity as satisfying the requirement is very rare and thus expensive.

On the other hand, it is known that diamond is after-treated under various states so as to improve the quality of the diamond. For example, as an after-treatment of diamond crystal grains used as abrasives for grinding diamond wheels, it has been proposed to improve the surface of raw material abrasives by a hydrogen plasma treatment as disclosed in Japanese Patent Laid-Open Publication No. 107088/1987 or to improve the toughness by separating and removing inclusions and then heating in a reducing atmosphere as disclosed in Japanese Patent Laid-Open Publication No. 165494/1995.

For use of jewels, it is known that defects are incorporated in a crystal by irradiation of rays, neutron, electron, etc. and then subjected to a heat treatment at a temperature of 300 to 800 °C to impart various colors thereto [“Genshi-Ryoku Kogyo (Atomic Energy Industry)”, Vol. 40 (1994), No. 7, page 71]. It is assumed that these treatments serve to restore a slight shift of carbon atom from the definite position by irradiation of electron ray. In the case of a large

shift of carbon atom from the definite position, exemplified by strain, however, there is no example of the restoration.

On the other hand, there are some reports for the purpose of changing crystallinity for uses of electronic materials. For example, Japanese Patent Laid-Open Publication No. 277176/1990 describes a method comprising forming a ring crack on the surface of a diamond crystal by an indentation member of a breakage tester, then subjecting it to a hydrogen plasma treatment at 600 °C and thus providing a number of crystal defects on the diamond surface to increase the emission intensity, Japanese Patent Laid-Open Publication No. 24990/1993 describes a method comprising subjecting a diamond crystal to a hydrogen plasma treatment after an oxygen treatment and thus improving the interface with a metal formed thereon to form a good Schottky contact, Japanese Patent Laid-Open Publication No. 144995/1994 describes a method comprising heating a diamond crystal in an oxygen atmosphere and thus removing a chief cause of hindering the insulation without damaging the diamond and Y. Mori: "Jpn J. Appl. Phys.", Vol. 31 (1992), L 1191 describes a method comprising implanting ion in the surface of a diamond crystal and then subjecting to a hydrogen plasma treatment to restore the breakage of the crystal when implanting ion. These examples aim at modifying only the surfaces of crystals and there is no example concerning improvement of crystallinity in the whole of a crystal.

Furthermore, it has been reported that diamond is deformed by heat-treating the diamond at a high temperature and high pressure, e.g. at least 7 GPa and at least 1000 °C. It is known that carbon atoms making up diamond can sufficiently be removed according to this method.

In the treatment at such a high pressure, however, there arises a problem that not only an expensive high pressure apparatus is required, but also defects are again incorporated into a diamond crystal bring the course of lowering the pressure and temperature to normal pressure and temperature.

Natural diamond has a number of defects or large strains in the interior part of the crystal. Natural type IIa diamond contains less impurities, but is not good as to the crystallinity such as defects, strains, etc. Thus, the natural type IIa diamond has a problem that it tends to be cracked during working and when applying to technical fields needing a strength as diamond, for example, an anvil for producing an ultra-high pressure, compression cell for FT-IR, laser window material, etc., it is readily broken in some case.

Further, it cannot be applied to a field needing high crystallinity, for example, monochromators, semiconductor substrates, etc.

On the other hand, a synthetic diamond, in particular, single crystal synthesized by the so-called temperature gradient method is much more excellent in crystallinity than natural diamond. The crystallinities of various diamond were estimated by the FWHM (full width at half maximum) of an X-ray diffraction rocking curve using Cu-K α as a source to obtain results as shown in the following Table 1.

Table 1

FWHM of Rocking Curve of Various Diamonds		
Diamond	Quantity of Nitrogen (ppm)	FWHM of Rocking Curve (arcsec)
Natural type Ia Diamond	~ 1000	7-60
Natural type IIa Diamond	< 1	200-2500
Synthetic type Ib Diamond	10-120	6-20
Synthetic type IIa Diamond	< 0.1	4-6

Herein, FWHM of a rocking curve is obtained by measuring an X-ray diffraction intensity curve (rocking curve) by the double crystal method using a synthetic diamond crystal (004) as a first crystal and searching for FWHM of this curve. If there are a number of defects or strains in a crystal, the rocking curve is broadened and thus a small FWHM teaches excellent crystallinity. It is apparent from Table 1 that both natural type Ia and type IIa diamonds have considerably many defects or strains and synthetic diamonds (synthesized by temperature gradient method) exhibit much higher crystallinity. Of synthetic diamonds, the synthetic type IIa can stably be obtained with high crystallinity because of being free from defects or strains due to nitrogen impurity.

Even in the case of the type IIa diamond synthesized by the temperature gradient method, however, the crystallinity is not complete and observing defects in the crystal by X-ray topography, a number of needle-shaped dislocation defects are found. The defect is one characteristic of the synthetic diamond, which also appears often in the synthetic type Ib diamond by the ordinary temperature gradient method. Because of the crystal defect, even the synthetic type IIa diamond cannot be applied to uses needing high crystallinity such as monochromators, semiconductor substrates, etc.

It is an object of the present invention to provide a high quality synthetic diamond single crystal with less defects or strains, whereby the disadvantages of the prior art can be addressed.

It is another object of the present invention to provide a process for the production of a transparent, high quality and good crystallinity synthetic diamond substantially free from impurities, crystal defects, strains, etc.

It is a further object of the present invention to provide a process for producing a low defect density synthetic diamond having a size of at least 0.1 carat, preferably at least 1 carat, which can effectively be applied to uses for electronic materials, in a relatively economical manner.

It is a still further object of the present invention to provide a process for the synthesis of a high quality and low defect density diamond single crystal having decreased needle-shaped defects and little strains.

These objects can be attained by a colorless, transparent low defect density, synthetic type IIa diamond single crystal, in which the etch pits due to needle-shaped defects are at most 3×10^5 pieces/cm² and a process for the production of the transparent low defect density synthetic diamond single crystal by growing new diamond crystal on a seed crystal of diamond by the temperature gradient method, which comprises using a crystal defect-free diamond single crystal as a seed crystal of diamond.

The accompanying drawings are to illustrate the principle and merits of the present invention in detail.

Fig. 1 is a schematic view of a distributed state of needle-shaped defects in the synthetic diamond crystal by the temperature gradient method.

Fig. 2 (s) is a schematic view of cutting planes (a), (b), (c) and (d) in a cross-section of the synthetic diamond crystal along (100) plane and Fig. 2 (a), (b), (c) and (d) are respectively distributed states of etch pits on the cutting planes.

Fig. 3 is a schematic view of the structure of a sample chamber for the synthesis of a diamond single crystal by the temperature gradient method.

The present invention is developed to solve the above described problems and thus provides a high quality synthetic diamond single crystal with lower defect density or strains, characterized by the following items:

- (1) A colorless, transparent low defect density, synthetic type IIa diamond single crystal, in which the etch pits due to needle-shaped defects are at most 3×10^5 pieces/cm².
- (2) The colorless, transparent low defect density, synthetic type IIa diamond single crystal, as described in (1), wherein the size is at least 0.1 carat.
- (3) The colorless, transparent low defect density synthetic type IIa diamond single crystal, as described in (1) or (2), wherein the crystal is applied to monochromators or semiconductor substrates.
- (4) A process for the production of the colorless, transparent low defect density, synthetic diamond single crystal, in particular, with a low nitrogen content, by growing new diamond crystal on a seed crystal of diamond by the temperature gradient method, as described in any one of (1) to (3), which comprises using a crystal defect-free diamond single crystal, as a seed crystal of diamond.
- (5) The process for the production of the colorless, transparent low defect density, synthetic diamond single crystal, as described in (4), wherein a diamond crystal free from crystal defects by X-ray topography is used as a seed crystal.
- (6) A process for the production of the colorless, transparent low defect density, synthetic diamond single crystal by growing new diamond crystal on a seed crystal of diamond by the temperature gradient method, as described in any one of (1) to (3), which comprises using a crystal defect-free diamond single crystal on at least the surface on which new diamond is grown, as a seed crystal of diamond.
- (7) The process for the production of the colorless, transparent low defect density synthetic diamond single crystal, as described in (6), wherein a diamond crystal having no crystal defects by X-ray topography on at least the surface on which new diamond is grown is used as a seed crystal.
- (8) The process for the production of the colorless, transparent low defect density, synthetic diamond single crystal, as described in (6), wherein a diamond crystal having no crystal defects by an etching test on at least the surface on which new diamond is grown is used as a seed crystal.
- (9) A process for the production of the colorless, transparent low defect density, synthetic diamond single crystal by growing new diamond crystal on a seed crystal of diamond by the temperature gradient method, as described in any one of (1) to (3), which comprises using a crystal defect-free piece cut from a diamond single crystal synthesized by the temperature gradient method as a seed crystal of diamond.
- (10) The process for the production of the colorless, transparent low defect density, synthetic diamond single crystal, as described in (9), wherein a diamond single crystal synthesized by the temperature gradient method is subjected to examination of the distributed state of crystal defects by X-ray topography and based on this examination result, a crystal defect-free part is cut from the diamond single crystal and used as a seed crystal.
- (11) The process for the production of the colorless, transparent low defect-density, synthetic diamond single crystal, as described in (9), wherein a diamond single crystal synthesized by the temperature gradient method is cut in the form of a plate, subjected to examination of the distributed state of crystal defects on the surface thereof by X-ray topography and based on this examination result, a crystal defect-free part on the surface is cut from the diamond single crystal and used as a seed crystal.
- (12) The process for the production of the colorless, transparent low defect density, synthetic diamond single

crystal, as described in (9), wherein a diamond single crystal synthesized by the temperature gradient method is cut in the form of a plate, subjected to examination of the distributed state of crystal defects on the surface thereof by an etching test and based on this examination result, a crystal defect-free part on the surface is cut from the diamond single crystal and used as a seed crystal.

5 (13) A process for the production of the colorless, transparent low defect density, synthetic diamond single crystal by growing new diamond crystal on a seed crystal of diamond by the temperature gradient method, as described in any one of (1) to (3), which comprises using a strain-free diamond as a seed crystal of diamond.

(14) The process for the production of the colorless, transparent low defect density, synthetic diamond single crystal, as described in (13), wherein such a diamond that strain is not found in the crystal by observation using a polarizing microscope is used as a seed crystal.

10 (15) A process for the production of a low defect density, synthetic diamond single crystal which comprises heat-treating the low defect-density synthetic diamond single crystal obtained by the process described in any one of (4) to (14) in a non-oxidizing atmosphere at a low pressure and a temperature of 1100 to 1600 °C.

(16) The process for the production of the low defect density, synthetic diamond single crystal, as described in (15), wherein the diamond single crystal before the heat-treatment is subjected to a treatment with hydrofluoric and nitric acid and/or the diamond single crystal after the heat-treatment is subjected to a treatment for removing graphite component.

(17) The process for the production of the low defect density, synthetic diamond single crystal, as described in (15) or (16), wherein the non-oxidizing atmosphere has an oxygen partial pressure of at most 10 Torr.

20 (18) The process for the production of the low defect density synthetic diamond single crystal, as described in any one of (15) to (17), wherein the non-oxidizing atmosphere is a plasma containing hydrogen.

(19) A process for the production of a low defect density, diamond single crystal, which comprises heat-treating a low defect diamond single crystal of at least 0.1 carat in a non-oxidizing atmosphere at a low pressure and a temperature of 1100 to 1600 °C.

25 (20) The process for the production of a low defect density, diamond single crystal, as described in (19), wherein the diamond single crystal before the heat-treatment is a synthetic type IIa diamond single crystal and/or a synthetic diamond single crystal whose crystallinity is at most 5 times as large as the theoretical FWHM of the X-ray diffraction intensity curve.

(21) The process for the production of a low defect density, diamond single crystal, as described in (19) or (20), wherein the diamond single crystal before the heat-treatment is subjected to a treatment with hydrofluoric and nitric acid and/or the diamond single crystal after the heat-treatment is subjected to a treatment for removing graphite component.

30 (22) The process for the production of a low defect density, diamond single crystal, as described in any one of (19) to (21), wherein the non-oxidizing atmosphere has an oxygen partial pressure of at most 10 Torr.

35 (23) The process for the production of a low defect density, diamond single crystal, as described in any one of (19) to (22), wherein the non-oxidizing atmosphere is a plasma containing hydrogen.

(24) A low defect density, diamond single crystal produced by the process as described in any one of (19) to (23).

40 In the type Ib having hitherto been prepared on a commercial scale, there are a number of causes of deteriorating the crystallinity. Above all, uneven distribution of nitrogen as an impurity largely affects the crystallinity, so whichever single crystal is used as a seed crystal, the crystallinity is not so changed.

In the case of the high purity type IIa diamond, having higher crystallinity, on the other hand, there is no influence of nitrogen and accordingly, the crystallinity is deteriorated by another cause. As a result of the inventors' examinations or researches, it is found that needle-shaped defects constitute a main factor of deterioration of the crystallinity. Thus, the inventors have made various studies on the cause of needle-shaped defects and consequently, have found that the needle-shaped defects in a synthetic diamond by the temperature gradient method almost come from a seed crystal part as a starting point. In Fig. 1 is shown a schematic state of needle defects obtained by observation using an X-ray topograph. As a seed crystal, there has commonly been used a synthetic diamond for abrasives, having a diameter of about 500 μm . Such a granular diamond has been synthesized by a method called film growth method, whereby only small diamond grains of 500 μm are obtained, and the thus obtained diamond grains each consist of a single crystal having a clear self-shape and is used as a seed crystal. However, it has been rendered apparent by an experiment of X-ray topograph that this diamond has much more crystal defects than the diamond synthesized by the temperature gradient method. The crystal defect of the diamond grain used as a seed crystal is considered to be one of causes of generating needle-shaped defects in the synthetic crystal by the temperature gradient method as shown in Fig. 1.

55 Thus, the inventors have considered it effective to use a seed crystal with less defects for the purpose of reducing the needle-shaped defects and consequently, have found that when a defect-free part is cut out of a single crystal once synthesized by the temperature gradient method and using this as a seed crystal, a type IIa diamond single crystal is

synthesized, there can be obtained a low defect density and high quality diamond having been synthesized up to the present time. The present invention is based on this finding.

Accordingly, the present invention provides a colorless, transparent low defect synthetic diamond single crystal, in which the etch pits due to needle-shaped defects are at most 3×10^5 pieces/cm², and a process for the production of the colorless, transparent low defect density, synthetic diamond single crystal by growing new diamond crystal on a seed crystal of diamond by the temperature gradient method, as described above, which comprises using a crystal defect-free diamond single crystal, as a seed crystal of diamond.

Estimation of the crystal defects in the seed crystal is preferably carried out by X-ray diffraction topography. In a diamond practically used as a seed crystal, there are various defects, for example, point defects such as pores, impurities, stacking faults, needle-shaped defects, dislocations, strains, etc. It is further found that unless, of these defects, there are those capable of being detected by X-ray topography, a good quality crystal can be obtained.

There are some methods called "X-ray topography", but in this case, a method called Lang's method can be used, for example, by using Mo-K α as an X-ray and photographing a diffraction image of (220) plane or (111) plane of a diamond crystal by a Lang's camera. The defects which can be confirmed by this method, depending on a photographing device, are in a range of upto about 5 μ m and the resolving power thereof can be maintained high in a range of upto about 1 μ m.

A seed crystal having only a surface part (growth surface) rendered free from defects can sufficiently be used and the estimation of defects on the surface of the seed crystal can simply be conducted in view of occurrence state of etch pits by etching as another method than the X-ray topography. Furthermore, the diamond single crystal synthesized by the temperature gradient method has partly a non-defect part which cannot be found in natural diamond and synthetic diamond grains by the film growth method and this non-defect part is preferably cut out for the use as a seed crystal. Before cutting, it is preferable to previously examine the distributed state of defects in the crystal or on the surface of the crystal by X-ray topography or etching test and based on the examination result, to cut a defect-free part out of the interior part or the surface of the crystal for the use as a seed crystal. It is also effective to use the seed crystal containing no strain inside the crystal and the strain in the seed crystal can readily be examined by a polarizing microscope. The etching test is ordinarily carried out by etching a diamond crystal in a crucible of platinum, etc. using a fused salt of KNO₃, etc. as an etching agent at a temperature of 600 to 700 °C for several minutes to several hours and examining the presence or absence of etch pits on the crystal surface by the naked eye.

When a diamond sample is cut along A-A cross-section shown in Fig. 1 and immersed in the above described fused salt, the distributed state of etching pits is given as shown in Fig. 2 (a). The distributed states of etch pits on surfaces cut along cross-sections (a), (b), (c) and (d) in Fig. 2 (s) are shown in Fig. 2 (a), (b), (c) and (d). The etch pits have the highest density in the central part and at the circumferential part, there are regularly arranged etch pits-enriched areas and etch pits-lean areas. It is herein to be noted that the density of etch pits just above the seed crystal is highest. The property of a low defect density, diamond single crystal is dependent on the density of etch pits on the above described high etch pit density area, i.e. etch pits-enriched area. In the present invention, therefore, the property of a diamond single crystal is generally estimated by the number of etch pits on the etch pits-enriched area. Thus, it is found that a diamond single crystal having etch pits in the range of at most 3×10^5 pieces/cm² can be applied to uses such as monochromators or semiconductor substrates.

As a method of improving the crystallinity of a single crystal, the single crystal has often been subjected to a heat treatment called annealing treatment. However, it has hitherto been considered in diamond that removal of defects or strains is difficult approximately under the atmospheric pressure because the bond energy among carbon atoms making up the diamond is larger.

However, the inventors have found, at the present time, that defects or strains included in diamond can partly be removed by carrying out a heating treatment in a non-oxidizing atmosphere at a temperature of 1100 to 1600 °C to raise the crystallinity and to obtain a diamond single crystal of at least 0.1 carat, excellent in crystallinity. This can be confirmed by reduction of FWHM of the diffraction intensity (hereinafter referred to as FWHM of X-ray) using the characteristic X-ray of molybdenum-K α_1 line (wavelength 0.709 nm).

It is known that at a temperature of lower than 1100 °C, a part of point defects is decreased, but the crystallinity is not so improved as confirmed by FWHM of X-ray. If the temperature exceeds 1600 °C, the strains are somewhat decreased, but graphitization proceeds so that the surface of the diamond is so roughened as not put to practical use.

As the diamond to be used for this heat treatment, it is required that solid impurity of the solvent, which is called "inclusion", is not included therein as in the case of type IIa and it is preferable that FWHM of X-ray before the heat treatment is at most 5 times as large as the theoretical FWHM. Of course, the low defect density, diamond single crystal obtained by the foregoing synthesis process can be applied to this heat treatment whereby to obtain a good quality diamond single crystal with decreased needle-shaped defects and little strain. When solid impurities are present in a diamond crystal to be heat-treated, strains or defects are rather increased, centered on the impurity, after the heat treatment due to difference in thermal expansion. When exceeding 5 times as large as the theoretical FWHM, impurities are contained in the crystal in many cases and there are a great number of defects or strains, so that FWHM of X-ray

is hardly changed even by the heat treatment.

FWHM of X-ray is used as a judgment standard of the crystallinity of diamond before the heat treatment. The kind of the X-ray used for measurement of FWHM is not particularly limited, but it is preferable to use an X-ray with a wavelength approximately equal to or shorter than that of the characteristic X-ray of molybdenum-K α_1 line (wavelength 0.709 nm) because of decreasing the measurement error.

The atmosphere for carrying out the heat treatment should be a non-oxidizing atmosphere and the partial pressure of oxygen is preferably adjusted to at most 10 Torr. Other components than oxygen are not particularly limited, but for example, inert gases such as nitrogen, argon, etc. and plasma containing hydrogen are preferably used. When the partial pressure of oxygen exceeds 10 Torr, graphitization or etching of the diamond surface rapidly proceeds to result in a roughened surface or deformation of the crystal shape. This is not preferable on practical use.

Depending on the time for the heat treatment, a plasma by a hydrogen-containing gas hardly etches a diamond surface at the above described temperature range. On the other hand, it can be assumed that the use of such a plasma serves to prevent graphitization and to result in recrystallization of the surface.

A diamond single crystal to be subjected to the heat treatment is preferably treated with hydrofluoric and nitric acids and the heat treatment method is not particularly limited. For example, there are used methods by microwave plasma heating, high frequency induction heating, infrared irradiation heating, resistance heating, etc.

After the heat treatment, it is preferable to conduct a treatment for removal of graphite component, for example, by treatments using chromic acid, a mixed solution of hydrofluoric acid and nitric acid, hydrogen plasma at a low temperature, etc. Even if using the hydrogen plasma atmosphere, a partial graphitization occurs on the uppermost surface by heating at a high temperature some times and in this case, a diamond single crystal with improved crystalline property can be taken by removal of the graphite.

The following examples are given in order to illustrate the present invention in detail without limiting the same.

Example 1

In Fig. 3 is shown a construction of a sample chamber (temperature gradient method) used for the synthesis of diamond. Synthetic diamond powder was used as a carbon source 1. High purity Fe and Co were used as a solvent 2 in a solvent proportion of Fe/Co = 60/40 (by weight) and about 4 weight % of carbon was added to prevent solubilization of a seed crystal. Further, 1.5 weight % of Ti was added to the solvent as a nitrogen getter. The seed crystal 3, in which crystal defects were not found by observation by X-ray topography, was prepared by cutting a piece of 0.5 x 0.5 x 0.3 mm from a type Ib diamond single crystal having a size of about 1 carat (diameter 5 mm), synthesized by the temperature gradient method. A graphite heater 5 was set to provide a temperature gradient of about 30 °C between the carbon source and seed crystal part and the raw material was exposed to a pressure of 5.5 GPa and a temperature of 1300 °C for 70 hours in an ultra-high pressure producing apparatus, thus growing diamond. 6 designates a pressure medium in Fig. 3. Consequently, a colorless and transparent good quality diamond single crystal (IIa) of about 1 carat, substantially free from inclusions, was obtained. Measurement of the nitrogen content in the crystal by ESR showed the presence of nitrogen in an amount of at most 0.1 ppm. When the product was subjected to measurement of visible ray, ultraviolet and infrared ray spectra, there were no absorptions due to other impurities than diamond itself. When the resulting diamond was observed by means of a polarizing microscope to estimate strains, it was found that there were little strains. When FWHM of X-ray diffraction rocking curve (X-ray source Cu-K α) by the double crystal method using the synthetic diamond crystal (004) plane as a first crystal was measured, it was 4.2 arcsec. Observation of defects in the crystal by X-ray topography taught that there were hardly found defects.

The diamond crystal was then immersed in a fused salt of potassium nitrate (KNO₃) at a temperature of 600 to 700 °C for 1 hour to count the number of etch pits formed on etch pits-enriched area, thus obtaining 2 x 10² pieces/cm².

Example 2

A type Ib diamond crystal synthesized by the temperature gradient method was sliced in a thickness of 0.3 mm, distribution of needle-shaped defects was observed by X-ray topography and a crystal piece of 0.5 x 0.5 mm was cut from the defect-free area and used as a seed crystal. The other procedures were carried out in the similar manner to Example 1 to synthesize a type IIa diamond crystal. Consequently, a high quality type IIa diamond crystal, substantially free from defects and similar to Example 1, was obtained. The density of etch pits on etch pits-enriched area was 3 x 10² pieces/cm².

Example 3

A type Ib diamond crystal synthesized by the temperature gradient method was sliced in a thickness of 0.3 mm and distribution of crystal defects was observed by X-ray topography. The sliced sample was treated with KNO₃ at 650

EP 0 715 885 A2

°C for 1 hour to etch the surface thereof. 3×10^6 pieces/cm² of etch pits were found on the area corresponding to the crystal defects observed by X-ray topography. A crystal piece of 0.5 x 0.5 mm was cut from the defect-free area (2×10^3 pieces/cm²) and used as a seed crystal. The other procedures were carried out in the similar manner to Example 1 to synthesize a type IIa diamond crystal. Consequently, a defect-decreased, high quality type IIa diamond crystal, having a mean etch pit density of 5×10^3 pieces/cm², was obtained.

Example 4

A type Ib diamond crystal synthesized by the temperature gradient method was sliced in a thickness of 0.3 mm and a crystal piece of 0.5 x 0.5 mm was cut from it. A sample, in which a transmission image due to strain was not found when observing by a polarizing microscope, was selected and used as a seed crystal. The other procedures were carried out in the similar manner to Example 1 to synthesize a type IIa diamond crystal. Consequently, a high quality type IIa diamond crystal, substantially free from defects, having a mean etch pit density of 2×10^4 pieces/cm², was obtained.

Example 5

The low defect density, type IIa diamond crystal synthesized in Example 1 was sliced in a thickness of 0.3 mm, a crystal piece of 0.5 x 0.5 mm was cut from it and used as a seed crystal. The other procedures were carried out in the similar manner to Example 1 to synthesize a type IIa diamond crystal. Consequently, a high quality type IIa diamond crystal, substantially free from defects and similar to Example 1, having a mean etch pit density of 1×10^2 pieces/cm², was obtained.

Comparative Example

Example 1 was repeated except using a commercially available synthetic diamond (diameter 0.5 mm) for abrasives as a seed crystal to synthesize a type IIa diamond crystal for estimation. The resulting diamond was a colorless, transparent type IIa diamond single crystal, having a size of about 1 carat, nitrogen impurity content of at most 0.1 ppm and no absorption due to impurities in ultraviolet, visible and infrared spectra. However, in the observation of strains by the use of a polarizing microscope, there was found some strains. When FWHM of rocking curve was measured, it was 5.8 arcsec, showing that the crystallinity was not so good. In the observation of defects in the crystal by X-ray topography, a number of needle-shaped defects were found. The etch pit density on etch pits-enriched area was 5×10^6 pieces/cm².

Example 6

A sliced sample of 1 mm x 1 mm x 0.5 mm from a type Ib diamond single crystal, having a size of about 1 carat, synthesized by the temperature gradient method, in which no crystal defect was found in the observation by X-ray topography, was chosen and subjected to etching in a fused salt of KNO₃. Thus, a sample having an etch pit density of about 5×10^2 /cm² was used as a seed crystal. High purity Fe and Co were used as a solvent in a solvent proportion of Fe/Co = 50/50 (by weight) and about 4 weight % of carbon was added to the solvent to prevent solubilization of the seed crystal. Further, 2.0 weight % of Ti was added to the solvent as a nitrogen getter.

Using an ultra-high pressure producing apparatus as shown in Fig. 3, the raw material was exposed to a pressure of 5.2 GPa and a temperature of 1320 °C for 60 hours thus growing diamond. Consequently, a colorless and transparent type IIa diamond single crystal, having a size of about 0.7 carat and with decreased needle-shaped defects, was obtained.

The resulting diamond crystal was heated in vacuum of 10^{-3} Torr at 1200 °C by microwave for 2 hours. The oxygen partial pressure was less than 10^{-3} Torr during the same time. The other procedures were carried out in the similar manner to the following Example 7 to prepare a sample for the estimation of crystallinity. The FWHM of the sample before the heat treatment was 1.8 arcsec., while FWHM of the sample after the heat treatment was 1.3 arcsec.

In this Example, there was obtained a good quality diamond single crystal with less needle-shaped defects and substantially free from strains, capable of being favorably applied to uses such as optical parts, spectroscopic crystals, monochromators, laser windows, anvils, semiconductor substrates, etc.

Example 7

This example is given for showing an improvement of the crystallinity according to the present invention. Estimation of the crystallinity was conducted utilizing (004) plane diffraction of diamond. Using MoK α characteristic X-ray (wave-

length 0.709 nm), the diffraction intensity curve by the double crystal method was measured to obtain FWHM. The theoretical FWHM by the double crystal method under the above described condition is about 1.0 arcsec. In addition, observation of strains by means of a polarizing microscope was carried out to obtain results shown in the following Table 2. Each of the samples used had a size of about 1 carat and was subjected to a heat treatment in an atmosphere of hydrogen, nitrogen or argon for 5 hours. The heating method was carried out using microwave plasma, resistance heating, etc. Each of the samples was washed with hydrofluoric and nitric acids before the heat treatment and subjected to a graphite removal treatment of the surface of a crystal with chromic acid after the heat treatment.

For comparison, the following samples were subjected to estimation of the crystallinity thereof:

1. Sample heated at 1000 °C.
2. Sample heated at 1650 °C.
3. Sample heat treated in an atmosphere whose oxygen partial pressure is 50 Torr.
4. Sample heated under such a state that solid impurities are contained.
5. Sample heated and not subjected to a graphite removal treatment.

Table 2 shows the kind of a single crystal diamond, presence or absence of impurities contained therein and heat treatment conditions, as to each of the samples.

Table 3 shows auxiliary treatments before and after the heat treatment, change of crystallinity by the heat treatment and the surface state.

Table 2

Sample	Kind of	Impurity	<u>Heat Treatment Conditions</u>				
No.	Diamond		Heating	Temper-	Atmos-	Total	Oxygen Partial
			<u>Method</u>	<u>ature</u>	<u>phere</u>	<u>Pressure</u>	<u>Pressure</u>
Example							
1	Art. IIa	no	Micro.	1100°C	H ₂	120Torr	< 10 ⁻³ Torr
2	Art. IIa	no	Micro.	1200°C	H ₂	120Torr	< 10 ⁻³ Torr
3	Art. IIa	no	Micro.	1600°C	H ₂	120Torr	< 10 ⁻³ Torr
4	Art. Ib	no	Micro.	1200°C	H ₂	120Torr	< 10 ⁻³ Torr
5	Art. Ib	no	Micro.	1500°C	H ₂	120Torr	< 10 ⁻³ Torr
6	Art. IIb	no	Micro.	1200°C	H ₂	120Torr	< 10 ⁻³ Torr
7	Natu. Ia	no	Micro.	1150°C	H ₂	120Torr	< 10 ⁻³ Torr
8	Natu. Ia	no	Micro.	1150°C	H ₂	120Torr	< 10 ⁻³ Torr
9	Art. IIa	no	Micro.	1100°C	H ₂	120Torr	10Torr
10	Art. IIa	no	Micro.	1300°C	H ₂	120Torr	1Torr

EP 0 715 885 A2

11	Art. IIa	no	Micro.	1100°C	H ₂	120Torr	< 10 ⁻³ Torr
12	Art. IIa	no	Micro.	1200°C	Ar	120Torr	< 10 ⁻³ Torr
13	Art. IIa	no	Resist.	1200°C	Air	< 10 ⁻³ Torr	< 10 ⁻³ Torr
14	Art. IIa	no	HF	1200°C	N ₂	120Torr	5Torr

Comparative

Example

1	Art. IIa	no	Micro.	1000°C	H ₂	120Torr	< 10 ⁻³ Torr
2	Art. IIa	no	Micro.	1650°C	H ₂	120Torr	< 10 ⁻³ Torr
3	Art. IIa	no	Micro.	1200°C	H ₂	120Torr	50Torr
4	Art. IIa	no	Resist.	1200°C	Air	250Torr	50Torr
5	Art. IIa	yes	Micro.	1200°C	H ₂	120Torr	< 10 ⁻³ Torr
6	Art. IIa	no	Micro.	1200°C	H ₂	120Torr	< 10 ⁻³ Torr

(Note) Art. IIa : artificial type IIa diamond

Natu. Ia : natural type Ia diamond

Micro. : microwave heating

Resist. : resistance heating

HF : high frequency induction heating

Table 3

Sample	Auxiliary Treatment		Measurement Results of Crystallinity				Surface
No.	Before	After	Before Heat		After Heat		State
	Heating	Heating	Treatment		Treatment		
			FWHM	Strain	FWHM	Strain	
			(arcsec.)		(arcsec.)		

Example

1	F.N. Acid	Chromic Acid	2.4	medium	1.8	little	flat
2	F.N. Acid	Chromic Acid	2.7	much	2.2	little	flat
3	F.N. Acid	Chromic Acid	2.0	little	1.6	no	flat
4	F.N. Acid	Chromic Acid	3.1	much	2.5	medium	flat
5	F.N. Acid	Chromic Acid	5.0	much	4.2	much	flat

6	F.N. Acid Chromic Acid	2.9	much	2.5	medium	flat
7	F.N. Acid Chromic Acid	2.7	medium	2.3	medium	flat
8	F.N. Acid Chromic Acid	3.7	much	3.3	much	flat
9	F.N. Acid Chromic Acid	2.2	little	1.8	no	flat
10	F.N. Acid Chromic Acid	2.4	medium	1.7	no	flat
11	F.N. Acid Chromic Acid	2.0	little	1.4	no	flat
12	F.N. Acid Chromic Acid	2.5	medium	2.2	little	flat
13	F.N. Acid Chromic Acid	2.7	much	2.4	medium	flat
14	F.N. Acid Chromic Acid	2.8	much	2.5	medium	flat

Comparative

Example

1	F.N. Acid Chromic Acid	2.6	much	2.6	little	flat
2	F.N. Acid Chromic Acid	2.9	much	2.4	medium	roughened
3	F.N. Acid Chromic Acid	2.4	medium	2.7	medium	roughened
4	F.N. Acid Chromic Acid	2.2	little	3.0	little	roughened
5	F.N. Acid Chromic Acid	2.3	medium	9.5	very much	flat
6	F.N. Acid no	2.0	little	2.2	little	blackened

(Note) F.N. Acid : fluoric and nitric acids

As is evident from the results of Tables 2 and 3, in Sample Nos. 1 to 14 having been subjected to the heat treatment within the scope with the feature of the present invention, the crystallinity is improved and a part or all of strains are removed. In Comparative Sample Nos. 1 to 6 not provided with the feature of the present invention, there is no improvement of the crystallinity, but rather, defects are increased.

Advantages of the Invention

The synthetic diamond single crystal of the present invention, having few impurities and little crystal defects and strains, can be applied to uses needing high crystallinity of diamond, for example, monochromators, semiconductor substrates, spectroscopic crystals in X-ray range, electronic materials, etc.

Claims

1. A colourless, transparent, low defect density synthetic type IIa diamond single crystal, having a density of etch pits due to needle-shaped defects of at most 3×10^5 pieces/cm².
2. A colourless, transparent, low defect density synthetic type IIa diamond single crystal as claimed in claim 1, wherein the crystal has a size of at least 0.1 carat.
3. A colourless, transparent, low defect density synthetic type IIa diamond single crystal as claimed in claim 1 or claim 2, wherein the crystal is used in a monochromator or as a semiconductor substrate.
4. A process for the production of a colourless, transparent, low defect density synthetic diamond single crystal as claimed in any one of claims 1 to 3, comprising growing new diamond crystal on a seed crystal of diamond by the

temperature gradient method, wherein the seed crystal comprises a diamond single crystal which is defect-free on at least the surface on which the new diamond is grown.

- 5 5. A process for the production of a colourless, transparent, low defect density synthetic diamond single crystal as claimed in claim 4, wherein the seed crystal is determined to be defect-free by X-ray topography or by an etch test.
- 10 6. A process for the production of a colourless, transparent, low defect density synthetic diamond single crystal as claimed in any one of claims 1 to 3, comprising growing new diamond crystal on a seed crystal of diamond by the temperature gradient method, wherein the seed crystal comprises a piece of defect-free crystal cut from a diamond single crystal synthesized by the temperature gradient method.
- 15 7. A process for the production of a colourless, transparent, low defect density synthetic diamond single crystal as claimed in claim 6, wherein the diamond single crystal synthesized by the temperature gradient method is subjected to an examination of the distributed state of crystal defects by X-ray topography and based upon the result of the examination the piece of defect-free crystal is cut from the diamond single crystal and used as the seed crystal.
- 20 8. A process for the production of a colourless, transparent, low defect density synthetic diamond single crystal as claimed in claim 6 or claim 7, wherein the diamond single crystal synthesized by the temperature gradient method is cut in the form of a plate, subjected to an examination of the distributed state of crystal defects on the surface thereof by X-ray topography or by an etching test and based upon the result of the examination the crystal defect-free part on the surface is cut from the diamond single crystal and used as the seed crystal.
- 25 9. A process for the production of a colourless, transparent, low defect density synthetic diamond single crystal as claimed in any one of claims 1 to 3, comprising growing new diamond crystal on a seed crystal of diamond by the temperature gradient method, wherein the seed crystal comprises a strain-free diamond.
- 30 10. A process for the production of a colourless, transparent, low defect density synthetic diamond single crystal as claimed in claim 9, wherein the seed crystal is determined to be strain-free by observation of the crystal using a polarizing microscope.
- 35 11. A process for the production of a low defect density synthetic diamond single crystal which comprises heat-treating either a low defect density synthetic diamond single crystal as obtained by the process claimed in any one of claims 4 to 10 or a low defect density diamond single crystal of at least 0.1 carat in a non-oxidizing atmosphere, at a low pressure and at a temperature in the range of from 1100 to 1600°C.
- 40 12. A process for the production of a low defect density synthetic diamond single crystal as claimed in claim 11, wherein the diamond single crystal prior to the heat-treatment is a synthetic type IIa diamond single crystal and/or a synthetic diamond single crystal having a crystallinity of at most 5 times as large as the theoretical FWHM of the X-ray diffraction intensity curve.
- 45 13. A process for the production of a low defect density synthetic diamond single crystal as claimed in claim 11 or claim 12, wherein the diamond single crystal is subjected to a treatment with hydrofluoric and nitric acids prior to the heat-treatment and/or the diamond single crystal is subjected to a treatment for removing a graphite component after the heat treatment.
- 50 14. A process for the production of a low defect density synthetic diamond single crystal as claimed in any one of claims 11 to 13, wherein the non-oxidizing atmosphere has an oxygen partial pressure of at most 10 Torr.
- 55 15. A process for the production of a low defect density synthetic diamond single crystal as claimed in any one of claims 11 to 14, wherein the non-oxidizing atmosphere is a plasma containing hydrogen.

FIG. 1

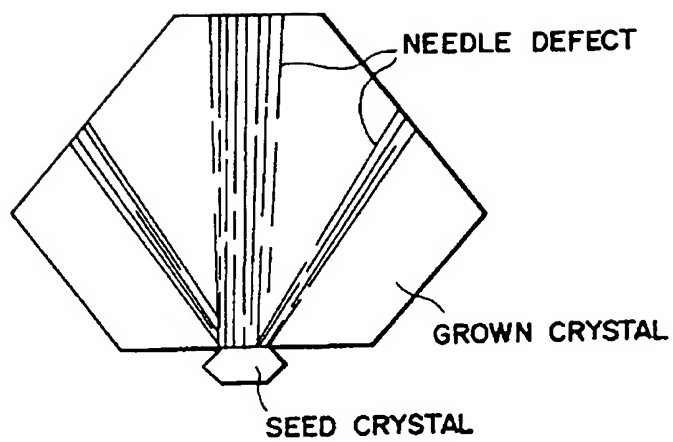


FIG. 2
(S)

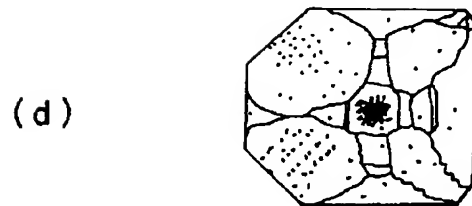
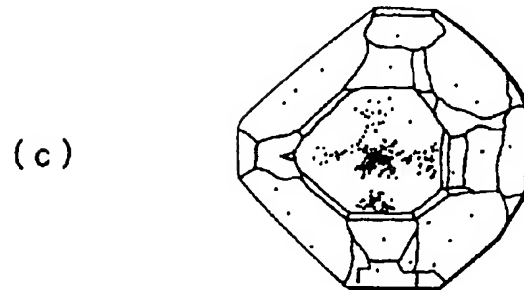
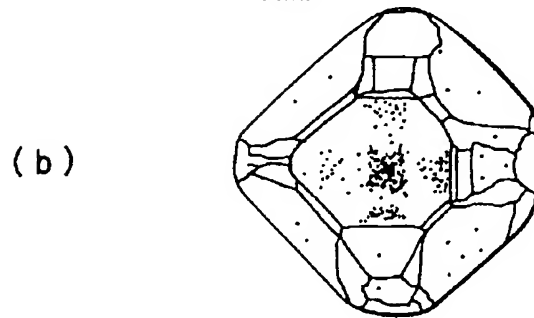
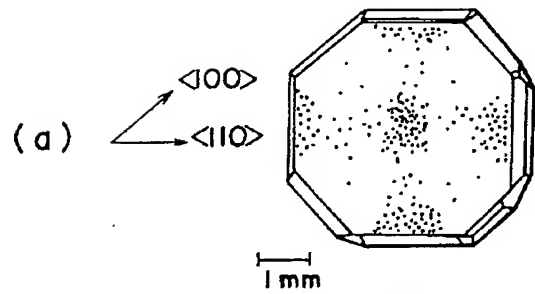
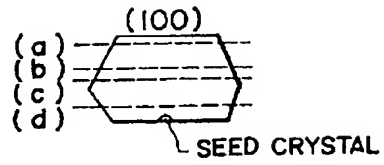


FIG. 3

